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(UGC Recognized NAAC Re- accredited 'A' grade state university)

"Synthesis and Characterization of Chemically Deposited $Co_{1-x}Mn_xFe_2O_4$ Thin Films for Electrochemical Supercapacitor Applications."

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Format for submission of Ph.D. Synopsis /Work plan

Abstract of proposed work plan / Problem:

"Synthesis and Characterization of Chemically Deposited $Co_{1-x}Mn_xFe_2O_4$ Thin Films for Electrochemical Supercapacitor Applications."

1. Introduction:-

Modern demands for electrical energy storage in terms of combining energy and power has stimulated research into a new class of charge storage materials called electrochemical supercapacitors [1-2]. Supercapacitors, applicable in several fields, such as hybrid electric vehicles, laser, fuel cells, cellular phones, digital camera etc., have been considered as a promising device improving the service life of batteries [3-5], Electrochemical capacitors are very interesting storage devices as they provide high power delivery required for many applications such as stop/go operation and regenerative braking of hybrid vehicles. These devices are generally called supercapacitors since they can deliver very high pulse power for limited time intervals with an acceptable capacity.

Thin film electrochemical supercapacitor represents the inter-mediate next generation energy storage device which is considered for high rate of charging/discharging, high power density and excellent chemical and environmental stabilities enabling its versatile use in electrochemical devices including electrical vehicles, power backup etc. [6]. Metal oxides are considered to be promising materials for electrochemical supercapacitors (ES). Among various metal oxide materials reported so far ruthenium oxide (RuO_2)is a major candidate for ES with a moderate value of specific capacitance (SC, 720 F/g) [7]. However, its high-cost and toxicity has made it difficult to find a commercial potential. Hence, alter- native inorganic electrode materials including manganese oxide [8], cobalt oxide [9], copper oxide [10], nickel oxide [11] vanadium oxide [12], tungsten oxide [13], iron oxide [14] etc., have intensively been investigated, owing to their readily availability, chemically stableness, mechanically robustness, safe, environmental friendlineness, and remarkably high performances in SC application [15–17]. The SC value of metal oxide can be enhanced, in general, by doping carbon nanotubes, graphene, polymers [18] etc. and in particular, mixing metal oxides of high catalytic activities [19]. The transition metal oxides are good electrode materials for ES application due their higher capacitance and fast redox reaction rate [20]. The iron oxide can react with divalent transition metal oxides MO (M-

metal) to form spinal ferrite (MFe_2O_4). Spinal transition metal oxides (AB_2O_4) with two metal elements provide the feasibility to tune the energy density and working voltage by varying the metal content [21-22]. Ferrites such as $MnFe_2O_4$ and $CoFe_2O_4$ have already had been corroborated good ES properties [23]. The different chemical methods like solvothermal [24], spray pyrolysis [25], reverse micelle technique [26], solid-state reaction [27], co-precipitation [28], sol–gel technique [29],hydrothermal [30], aerosolization [31], microwave hydrothermal [32], ultrasonic–hydrothermal [33], sonochemistry [34] and ball milling [35-36], etc., are being addressed for fabricating ferrite materials either in powder or directly in thin/thick film categories.

To the best of our knowledge, for electrochemical supercapacitor applications very few reports have been focused on $Co_{1-x}Mn_xFe_2O_4$ thin films using a cost effective chemical technique.

Preparation of good quality $Co_{1-x}Mn_xFe_2O_4$ thin films

It is proposed to synthesize $Co_{1-x}Mn_xFe_2O_4$ thin films by chemical method (chemical bath deposition / spray Pyrolysis). Initially the good quality $Co_{1-x}Mn_xFe_2O_4$ thin films will be deposited on glass and conducting glass substrates. The various preparative parameters like concentration of the ingredients, deposition temperature, thickness and other parameters will be optimized to get good quality $Co_{1-x}Mn_xFe_2O_4$ thin films. They as deposited thin films will be characterized by various characterization techniques in the following manner.

[A] Structural Analysis:

An X-ray diffraction technique will be employed to know the structural changes as a result of Mn incorporation into $CoFe_2O_4$. The interplanar distance (d), intensities of reflections, lattice constants and crystal dimension will be examined and their dependence on composition will be studied.

[B] Compositional Analysis:

The compositional analysis will be done by means of an EDAX or EDS technique and correlation will be made with as taken and observed contents of $Co_{1-x}Mn_xFe_2O_4$ thin films.

[C] Microscopic Studies:

To study the surface morphological features SEM/TEM/AFM technique will be utilized. The crystallographic and morphological information will be used to explain the transport mechanism and optical properties.

[D] Optical Properties:

The optical constants viz optical absorption coefficient (α), the energy band gap (E_g) and mode of optical transition will be determined from optical studies. For this purpose optical absorption / transmission / reflection spectra of the as deposited $Co_{1-x}Mn_xFe_2O_4$ series will be studied.

[E] Electrical transport properties:

The electrical conductivity and thermo-electric power will be measured of all these as deposited thin films. Various terms like carrier concentration (n), mobility (μ), activation energy (E_a) and barrier height (ϕ_B) will be determined.

[F] Electrochemical characterization:

Electrochemical capacitors (*i.e.* supercapacitors) include electrochemical double-layer capacitors that depend on the charge storage of ion adsorption and pseudo-capacitors that are based on charge storage involving fast surface redox reactions. The energy storage capacities of supercapacitors are several orders of magnitude higher than those of conventional dielectric capacitors, but are much lower than those of secondary batteries. They typically have high power density, long cyclic stability and high safety, and thus can be considered as an alternative or complement to rechargeable batteries in applications that require high power delivery or fast energy harvesting. The following electrochemical characterization will be undertaken

1. Cyclic voltammetry
2. Galvanostatic charge discharge studies
3. Electrochemical impedance spectroscopy

[G] Effect of technical parameter:

To boost the electrode performance effect of technical parameter such as material thickness / heat treatment / impurity concentration will be undertaken.

2. Review of Literature and Development in the subject

The recent research completed on nanostructured materials with unique properties in terms of electrode conductivity and grain-to-grain contacts. This can directly influence the equivalent series resistance (ESR) of the cell. Thus nano sized particles enable as best electrode to achieve high rate capability within the cell.

Tang *et al.* [37] prepared hierarchical hollow manganese oxide nanospheres with both a large surface area and a layered structure by a templating assisted hydrothermal process exhibited an ideal capacitive behavior and good cycling stability in a neutral electrolyte system with 299 Fg^{-1}. Lin *et al.* [38] reported a new type of asymmetric supercapacitor containing a $MnFe_2O_4$ negative electrode and a $LiMn_2O_4$ positive electrode in aqueous electrolyte has been synthesized and characterized. The nanocrystalline $MnFe_2O_4$ anode material has a specific capacitance of 99 F g^{-1} and the $LiMn_2O_4$cathode a specific capacity of 130-100 mAh g^{-1} under 10-100 C rate. The cell has a maximum operating voltage window of 1.3 V, limited by irreversible reaction of $MnFe_2O_4$ toward reducing potential. The specific power and specific energy of the full-cell increase with increasing anode-to-cathode mass ratio (A/C) and saturate at A/C-4.0, which gives specific cell energies, based on total mass of the two electrodes, of 10 and 5.5 $Whkg^{-1}$ at 0.3 and 1.8 $kWkg^{-1}$, respectively. The cell shows good cycling stability and exhibits significantly slower self-discharge rate than either the $MnFe_2O_4$symmetric cell or the other asymmetric cells having the same cathode but different anode materials, including activated carbon fiber and MnO_2.

Wang *et* a/. [39] reported reduced graphite oxide-$CoFe_2O_4$ (RGO-$CoFe_2O_4$) composites were synthesized by adding different amounts of $CoFe_2O_4$ into a mixed aqueous solution of graphite oxide, $Co(NO_3)_2$ and $Fe(NO_3)_3$ at room temperature. $NH_3.H_2O$ was used to adjust the synthesis system's pH value. Capacitive properties of the synthesized electrodes were studied using CV and EIS in a three-electrode experimental setup using 1 M Na_2SO_4 aqueous solution as electrolyte. It is found that the pH value plays an important role in controlling the electrochemical properties of these electrodes. Among the synthesized electrodes, RGO-$CoFe_{10}$ (pH ~10) shows the best capacitive properties because of its suitable particle size and good dispersion property. It could be anticipated that the synthesized electrodes will gain promising applications as novel electrode materials in ECs and other devices by virtue of their outstanding characteristics of controllable capacitance and facile synthesis.

3. Objectives of Research/Proposed Hypothesis

Following are the objectives of our research work

1. To deposit good quality $Co_{1-x}Mn_xFe_2O_4$ (x = 0 to 1) thin films by chemical route.
2. To study various properties such as thickness, optical, electrical properties of as deposited samples.
3. To study micro-structural and morphological features of as grown $Co_{1-x}Mn_xFe_2O_4$ thin films.
4. To use these films in supercapacitor applications and study their electrochemical characteristics.
5. To study the effect of technical parameter on Supercapacitive performance of optimum samples of $Co_{1-x}Mn_xFe_2O_4$.

4. Methodology to be adopted:

The chemical method will be used to synthesize the $Co_{1-x}Mn_xFe_2O_4$ thin films. Unlike the physical methods of preparation of thin films involving evaporation or ejection of material from a source, chemical methods of thin film deposition entail a definite chemical reaction. The chemical method is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipments. The starting chemicals are commonly available and cheap. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained.

In our present work, $Co_{1-x}Mn_xFe_2O_4$ thin films will be prepared by a chemical method. The deposited thin films will be characterized to study the structural, morphological, optical and electrical properties by means of XRD, SEM, UV-Vis spectrophotometer/FTIR respectively. The Supercapacitive properties of $Co_{1-x}Mn_xFe_2O_4$ thin films will be studied.

5. Importance of study / Society applications:

Now a day, we are in need of storage devices with improved storing capacity to store energy, when it is available and regain when it is needed. Electrical energy storage devices are essentially required in several applications such as electric hybrid vehicles, standby power systems and telecommunication devices (cell phones, remote communication, walkie-talkies etc.) in the form of storage components (batteries, supercapacitors and fuel cells) [40].

Supercapacitors are used to improve battery and capacitor performance in terms of power and energy density, respectively. Batteries can provide extremely high currents and can discharge very slowly when short-circuited, which means a large amount of energy can store in batteries but charge up within hours. On the other hand, capacitors can deliver more power but discharge very rapidly to store less energy compared to batteries. In future planning it is needed to store large amount of electricity, we will turn to supercapacitors that combine the best of batteries and capacitors. In addition, electrochemical capacitors are expected to have a much longer cycle life than batteries because of no or negligibly small chemical charge transfer reactions are involved [41].

6. Proposed work Plan / Formulation and Structure of Study:

Year-wise plan of work and targets to be achieved

Year I-Plan:

In the first year of the research literature survey and data collection will be done in order to get more information about work already done and scope of the present work. The literature survey includes collection of Journals, books, and related research papers. The chemicals of high purity will be purchased and efforts will be made to deposit good quality $Co_{1-x}Mn_xFe_2O_4$ thin films. At the end of the year two progress reports will be submitted.

Year II-Plan:

In second year, all preparative parameters will be optimized in order to get good quality thin films of $Co_{1-x}Mn_xFe_2O_4$ on conducting glass substrates. The as deposited films will be characterized by various characterizing techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis by X-ray (EDAX), UV-Vis photo spectrometer/FTIR and Supercapacitive study. The results will be analyzed and efforts will be made to publish two or more research papers in reputed research journals. Two progress reports will be submitted at the end of this year.

Year III-Plan:

In the last year, an optimum composition yielding better result will be searched out and effect of technical parameter such as material thickness / heat treatment / impurity concentration will be studied. The results obtained will be analyzed and an attempt will be made to publish it in the reputed journals. Also efforts will be made to share results in the national and international

Seminars, Conferences and Workshops etc. during this year. At the end of the year other progress reports will be submitted.

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